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Thermoelectric properties of tungsten ceramics prepared from nanopowder precursors

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Tungsten trioxide ceramics were prepared from nm-sized powder precursors. Thermoelectric properties of samples were investigated. The results demonstrated that ceramics prepared in this manner have improved electrical conductivity and Seebeck coefficient values. The power factor of these samples also improved markedly, the largest power factor being 0.027 μW m^{-1} K^{-2} at 773 K.

nanopowders, electrical conductivity, Seebeck coefficient, powder factor, tungsten trioxide

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Thermoelectric materials that convert heat into electrical energy directly have attracted much attention recently, driven by demands for clean energy sources and device coolers [1,2]. For this purpose, thermoelectric materials with high energy-conversion efficiency are widely sought. In 1997, Terasaki et al. [3] first reported the discovery of layered p-type cobalt oxides that had comparable figure of merit to conventional materials. Since then, attention has focused on metal oxides. Recently, metal oxides have been exploited as candidates for applications in thermoelectric generation because of their thermal and chemical stability in air at high temperature, oxidation resistance, reduced toxicity, easy manufacture, and low cost [4–9].

We have studied the thermoelectric properties of tungsten trioxide (WO_3) [10–12] in recent years. As is well-known, the electrical conductivity and thermoelectric properties of WO_3-based ceramics prepared by μm-powders is quite low; if these ceramics are to play a role, the thermoelectric properties of WO_3 require further research and improvement. With this aim, those properties of tungsten ceramics prepared from nanopowders rather than μm-powders have for the first time been investigated. We found that the thermoelectric performance of the new ceramics can be improved markedly.

H_2WO_4 and citric acid were added to liquid ammonia, and the solution was magnetically stirred for 10 h to produce a yellow colored colloidal solution. This solution was placed in an infrared baking oven and baked until it became a black gelatum. The gel was sintered at 823 K for 2 h at a rate of heating of 3°C min^{-1} and cooled in the furnace to produce the nanometer tungsten trioxide powders. After milling in a mortar of agate for 5 h, the mixed powder was pressed into wafers 10 mm in diameter and 1.2 mm thick under a pressure of about 300 MPa. The pellets were sintered in a muffle furnace at 1000°C for 1 h in air.

The surface microstructure of the composite was examined using a scanning electron microscope (SEM, FEI QUANTA200, Netherlands). For the SEM analysis and Energy Dispersive X-Ray Spectroscopy (EDX), the samples were cleaned with acetone, mounted, and gold-coated to prevent charging. The crystalline phases of the sintered sample were identified using a X-ray diffractometer (XRD, 7602 EA Almelo, Netherlands) under the following experimental conditions: Cu Kα, λ=0.15406 nm, 40 kV, 40 mA,

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$20° \leqslant 2\theta \leqslant 60°$. The electrical conductivity and thermoelectric power over the temperature range from 300 to 773 K were calculated from thermoelectric voltage data (Series 2400, Keithley Instruments, Cleveland, OH) and the temperature difference between the two ends of the sample.

A SEM micrograph (Figure 1) of a WO_3 ceramic prepared from nanopowders shows that the grain size of the sample is about 1 μm, smaller than the samples prepared with μm-powders. The phase structure of the samples is shown in Figure 2. The JCPDS database of crystallographic entries suggest that the triclinic (δ-WO_3) and monoclinic (γ-WO_3) phases of WO_3 are coexisting. The result is similar to the undoped samples prepared from μm-powders [13].

The temperature dependence of the electrical conductivity (σ) for the sample (see log-normal plot in Figure 3) indicate that the curves of lnσ against 1000/T exhibit near linear characteristics for T>300°C, suggesting approximately semiconductive behavior. However, the variation in the electrical properties for T<300°C does not obey Arrhenius' law:

$$\sigma = \sigma_0 \exp\left(-\frac{E_\alpha}{kT}\right),$$

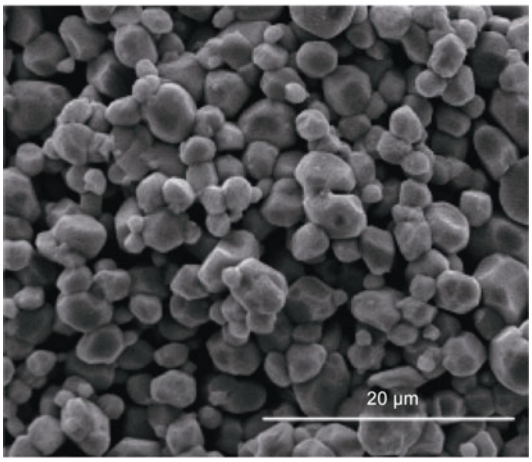

Figure 1 SEM micrograph of tungsten trioxide ceramic prepared from nanopowder.

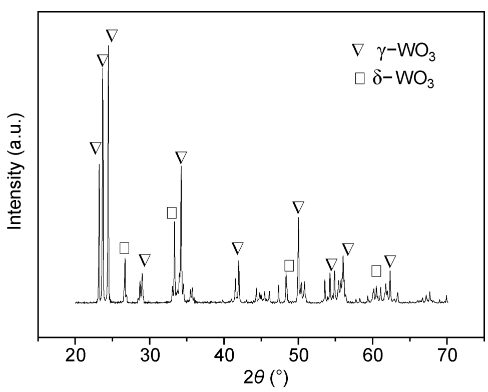

Figure 2 XRD patterns of the sample.

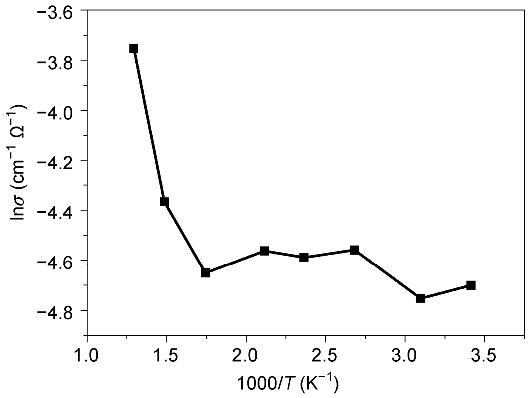

Figure 3 Temperature dependence of the electrical conductivity of the sample.

where σ is the electrical conductivity, σ_0 is a constant, k is the Boltzmann constant, T is the absolute temperature, and E_α is activation energy. Clearly, an important change in the electrical characteristics is occurring in the ceramics as temperature increases above room temperature; other physical processes are influencing electrical transport besides heat activation. The variation of the activation energy is due to the WO_3 phase transition at temperatures of about 300°C where 1000/T is 1.7 K^{-1}. The result also demonstrates that the electrical conductivity of the sample prepared from nanopowders is two orders of magnitude greater than the sample prepared from μm-powders [10].

Figure 4 presents the temperature dependence of the Seebeck coefficient (S) for the sample. The absolute value of S increases as temperature increases, but its values are all negative over this temperature range, indicating n-type conduction. In general, the Seebeck coefficient decreases with increasing electrical conductivity [8,14]. According to a simplified broadband model, the Seebeck coefficient for extrinsic n-type semiconductor devices with negligible hole conduction can be expressed as [15]: $S = -(k/e)[\ln(N_v/n)+A]$, where k is the Boltzmann constant, n is the electron concentration, e is the electric charge of the carrier, N_v is the density of state, and A is a transport constant, typically $0 \leqslant A \leqslant 2$.

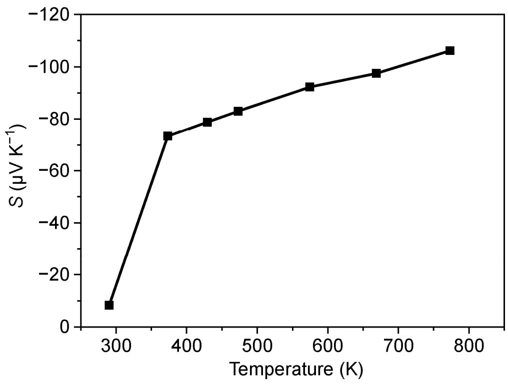

Figure 4 Temperature dependence of the Seebeck coefficients of the sample.

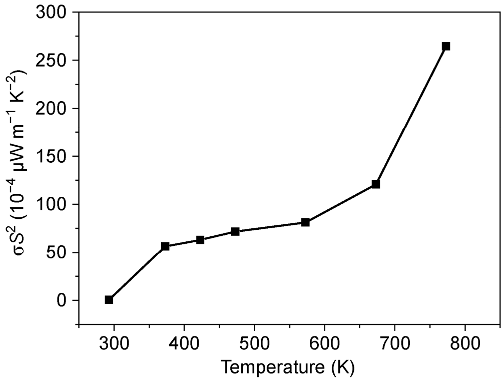

Figure 5 Temperature dependence of the power factor of the sample.

In general, with increasing electrical conductivity, the Seebeck coefficient decreases [8,16]. Moreover, grain size also affects the value of the Seebeck coefficient. Gao et al. [17] reported that the Seebeck coefficient increased as size decreased. The largest value for the Seebeck coefficient is −106.2 μV K^{-1}, which is larger than the samples made by μm-powder [11].

From Figures 3 and 4, we see the electrical conductivity and the Seebeck coefficient of the sample prepared from nanopowders were larger than that prepared from μm-powders [10–12]. A plot of the thermoelectric power factor (σS^2) of the sample, as a function of temperature (Figure 5) shows enhancement as temperature rises. At 773 K, the sample attains its largest power factor, 0.027 μW m^{-1} K^{-2}.

The thermoelectric properties of WO_3 ceramics prepared from nanopowders have been investigated. The results demonstrate that the electrical conductivity and the Seebeck coefficient are higher than for undoped ceramics prepared from μm-powders. The sample obtains its largest power factor of 0.027 μW m^{-1} K^{-2} at 773 K. Thus, nanopowder preparations can provide improved thermoelectric properties of WO_3 ceramics that might offer superior candidates for applications in thermoelectric generation.

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